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(54) Title: DIESEL FUELS

(57) Abstract

A fuel-soluble composition suitable for use in an automotive diesel engine comprises (A) at least one diesel detergent and (B) at least one cetane improver. Such composition can be used for reducing wear on cylinder liners, piston rings and rotary fuel injection pumps of diesel engines.

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DIESEL FUELS

The present invention relates in general to diesel engines, and in particular automotive diesel engines, and to fuels therefor.

A problem observed in connection with diesel engines is wear to the cylinder liners and piston rings which eventually leads to increased oil consumption. Another problem observed with diesel fuel containing less than 0.05% sulphur is wear in fuel injection pumps.

We have now found that a solution to the problem is to incorporate into the diesel fuel certain additives.

Therefore according to the present invention there is provided a fuel-soluble composition suitable for use in an automotive diesel engine comprising, (A) at least one diesel detergent and (B) at least one cetane improver.

According to a further aspect of the present invention there is provided the use of a fuel-soluble composition for reducing the wear on cylinder liners, piston rings and rotary fuel injection pumps of diesel engines wherein the composition comprises (A) at least one diesel detergent and (B) at least one cetane improver.

Diesel fuels are well known in the art and the man skilled in the art would understand what is meant by the expression diesel fuel. It is with automotive diesel fuels that this invention is concerned. In particular automotive diesel fuels are typically middle distillate fuel oils which generally boil in the range 150 to 400°C for example 170 to 350°C. The automotive diesel fuel will be comprised of several hydrocarbon fractions. It is preferred that at least 90% preferably greater than 95% volume of the fuel would be recovered on distillation at 350°C, and at least 15% preferably up to 10% volume would be recovered on distillation at 180°C. The aromatic content of an automotive diesel fuel would typically be less than 40% volume, preferably less than 30% more preferably less than 20%. The cetane number of an automotive diesel fuel

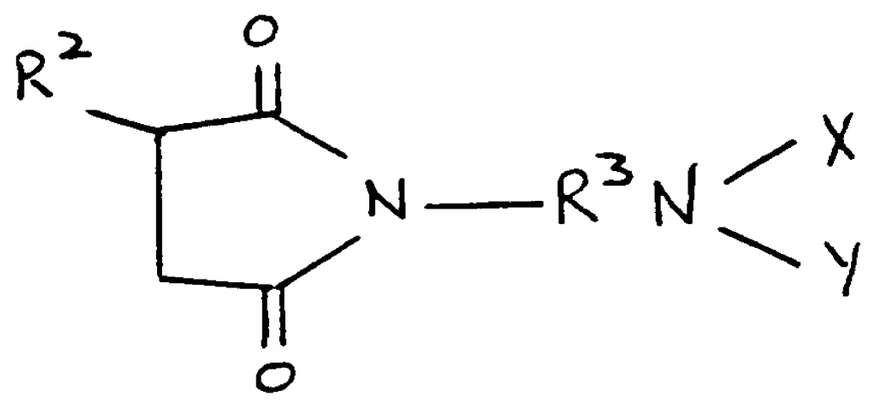
will generally be greater than 40, preferably greater than 45, more preferably greater than 50. In addition, the sulphur content of automotive diesel fuels is generally less than 0.5% preferably less than 0.2 more preferably less than 0.05% w/w. It is a feature of the present invention that the sulphur content of the fuel can be reduced significantly without adverse wear performance by using the defined additive package.

Although the present invention is particularly concerned with automotive diesel fuel, its scope nevertheless would also cover diesel fuel for use in railroad, and static diesel engines and either direct or indirect injection engines. Where the diesel engine is an automotive engine, the engine capacity will typically vary between 1 and 4 litres for cars and between 2 and 20 litres for trucks.

The fuel-soluble composition of the present invention comprises (A) at least one diesel detergent, and (B) at least one cetane improver. The term 'diesel detergent' includes all those materials which would be suitable for use in diesel engines and which have detergent action, generally classified as dispersants which have detergency action. Detergency in diesel engines is generally associated with a range of amine type detergents and polymeric dispersants typified by the following compounds:- amines, imidazolines, amides, fatty acid succinimides, polyalkylene succinimides, polyalkylene amines and polyether amines. Preferred detergents are (i) oil-soluble amides or imides of long-chain hydrocarbyl-substituted mono- and dicarboxylic acids or their anhydrides and (ii) long-chain hydrocarbyl monoamine or polyamine.

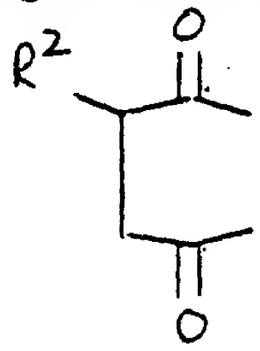
Succinimides are a well-known class of detergent. Typical of the art relating to such materials is GB-A-1565627 and the prior art acknowledged therein. Typically, they are prepared by reacting a polyalkene, in the presence or absence of chlorine, with either maleic acid, or preferably maleic anhydride, to produce a polyalkene-substituted succinic acid or anhydride and thereafter reacting the polyalkene-substituted succinic acid or anhydride with a nitrogenous material, suitably an amine, which may be a mono-, di- or polyamine.

A suitable succinimide has the formula:-



(I)

wherein R^2 is a hydrocarbyl group, typically a polyolefin group, preferably containing between 30 and 300 carbon atoms, more preferably between 50 and 150 carbon atoms; R^3 is a divalent group such that H_2NR^3NXY is an alkylene amine, such as an ethylene or propylene amine, (for example R^3 is $-(CH_2CH_2NH)_kCH_2CH_2$ wherein k is zero or an integer from 1 to 7, preferably 2 to 6), or a mixed ethylene/propylene amine, for example $H_2N(CH_2)_3NH(CH_2)_2NH(CH_2)_3\ NH_2$; and X and Y are independently either hydrogen, alkyl, or hydroxy alkyl, each of 1-6 carbon atoms, e.g. methyl, ethyl or hydroxyethyl, or together form the group:-



(II)

Alternatively, R^3 in the formula (I) may be a divalent group such that H_2NR^3NXY is an alkanolamine or a polyether amine. Typically such alkanolamines may contain the group $=N.CH_2CH_2NH.CH_2CH_2OH$ (i.e. $R^3 = CH_2CH_2$; X = H; Y = CH_2CH_2OH) and typically such polyether amines may contain the group $=NCH_2CH_2OCH_2CH_2.OCH_2CH_2NH_2$ (i.e. $R^3 = (CH_2CH_2O)_2CH_2CH_2$; X = Y = H). Useful commercially available polyether amines are the Jeffamines (RTM) marketed by Texaco. R^3 is preferably an alkylene group, e.g. of 2 to 40 carbon atoms, optionally interrupted with at least one -O- or =NH group and in particular contains one or more units of alkylene oxa or alkylene amino groups, each of 2-4 carbon atoms.

R^3 may also be a divalent group such that H_2NR^3NXY is an aromatic or araliphatic amine, e.g. of 6-20 carbon atoms, such as phenylene or biphenylene diamine or bis(amino benzyl).

Suitably in the formula (I) R^2 is a polyalkene group derived from either ethylene, propylene, l-butene, isobutene, l-hexene, l-octene, and the like. Alternatively, the polyalkene may be derived from an internal olefin, e.g. 2-butene, or an interpolymer, e.g. an ethylene/propylene copolymer. Preferably the polyalkene is a polyisobutene.

The succinimide may be either a mono- or a bis-succinimide.

Alternatively, the detergent can be a long-chain hydrocarbyl monoamine or polyamine. Such monoamines include monoamines having the general formula

$$ABNR^4 \qquad \text{III}$$

where A and B are independently hydrogen, a hydrocarbyl group of from 1 to about

10 carbon atoms, for example Me or Et or hydroxyhydrocarbyl group of from 1 to about 10 carbon atoms for example $-CH_2OH$ or $-CH_2CH_2OH$; R^4 is an aliphatic hydrocarbyl group of from about 30 to 400 carbon atoms (e.g. polyisobutyl). PIB amines are particularly preferred as such monoamines. Alternatively the detergent can be a polyamine of the formula $ABN(R^5N)_nR^4$ (IV) where A,B and R^4 have the meanings given to them as hereinabove, R^5 is a divalent group such as an alkylene group or oxyalkylene group, and n is an integer, for example n=1-7 preferably 2-4. R^5 is preferably $-CH_2CH_2-$ or $-OCH_2CH_2-$. Where n=0, the compound of formula IV is a monoamine.

Diesel detergents are sold in various additive packages marketed by several additive manufacturers. In general the additive packages available appear to be based on compounds which can be classified as polymeric dispersants. The high viscosity of these compounds generally dictates that they are distributed in diluted form, typically 50% or more of an aromatic kerosene diluent being used. Any of the commercially available detergents may be employed.

The amount of detergent employed may be sufficient to provide up to 1000 ppm, for example up to 500 ppm, typically up to 250 ppm in the fuel.

As regards the cetane improver (B), these are materials which promote fast oxidation of fuels and thus improve their ignition characteristics. Typical cetane improvers include the alkyl nitrates, ether nitrates, dinitrates of polyethylene glycols and certain peroxides. In general, however, in view of their low cost and ease of handling, primary alkyl nitrates are preferred. Examples of suitable cetane improvers useful in the performance of the invention include iso-propyl nitrate, iso-amyl nitrate, iso-hexyl nitrate, cyclohexyl nitrate and iso-octyl nitrate. A preferred cetane improver is iso-octyl nitrate.

As a supplement to adding a cetane improver of the aforesaid type the cetane number of the fuel may be increased by the addition of a hydrocarbon fraction known to be beneficial to ignition quality, for example a paraffinic hydrocarbon fraction.

In addition to the components (A) and (B) the fuel-soluble composition preferably incorporates as component (C) a demulsifier for fuel-water emulsions. Any of the commercially available demulsifiers may be employed, suitably in an amount sufficient to provide a treat level of from 5 to 50 ppm in the fuel. A class of suitable demulsifiers are the quaternary ammonium salts.

The fuel-soluble composition preferably further incorporates as component (D) an antioxidant. Antioxidants are useful for inhibiting gum formation during fuel

storage. Diesel antioxidants in current use are mainly based on hindered phenol or amine structures. Any of the commercially available diesel antioxidants may be employed, suitably in an amount sufficient to provide a dose rate of from 2 to 200 ppm in the fuel.

Finally, the fuel-soluble composition may suitably incorporate a liquid carrier for the components (A) and (B) and optionally (C) and (D). Suitable carriers include liquid hydrocarbons, for example kerosene. Alternatively, diesel fuel itself may be used as a carrier.

The fuel-soluble composition may be incorporated into the fuel during its manufacture.

Alternatively the composition may be blended into additive-free fuel contained in the fuel storage tanks of individual vessels.

In a further aspect of the present invention, there is provided a diesel fuel composition comprising a major amount of a diesel fuel and a minor amount of the fuel-soluble composition as hereinbefore described.

In another aspect of the present invention, there is provided a method of reducing engine wear in diesel engines and fuel injection pumps, in particular automotive diesel engines operating on diesel fuels comprising adding to the diesel fuel a fuel-soluble composition comprising at least one diesel detergent and at least one cetane improver.

The invention will now be illustrated with reference to the following Examples.

Example 1

The results of four MWMKD 12E engine tests in respect of piston cleanliness., oil consumption, piston ring and cylinder wear, bore polishing and (wear) elements in the used oil are given in Table I for an automotive diesel fuel having sulphur content of 0.03% and with and without A1052D, a diesel fuel additive package comprising (A) a diesel detergent and (B) a cetane improver.

Example 2

The results of tests with rotary fuel injection pumps in respect of the wear effect are given in Table II for two automotive diesel fuels having sulphur contents of 0.03% and 0.002% with and without A1052D, a diesel fuel additive package comprising (A) a diesel detergent and (B) a cetane improver.

Table I

	Diesel Fuel	
Criterion	With A1052D	Without A1052D
Piston Cleanliness	73 68	61 62
Oil Consumption (g)	1108 1208	1198 1388
Piston Ring Wear (g)	0.0493 0.0494	0.0585 0.0749
Cylinder Wear	1.5 1.7	2.4 2.6
Bore Polishing (%)	0.9 0.8	1.8 3.0
Wear Elements in used Oil: Iron (mg/kg)	169 143	205 227
Chromium (mg/kg)	4 4	10 6

Table II

Wear Criterion	Diesel Fuel		Sulphur content of fuel w %
	With A1052D	Without A1052D	
% Increase in fuel flow	4 3	12 15	0.03 0.02

Claims

1. A fuel-soluble composition suitable for use in an automotive diesel engine comprising (A) at least one diesel detergent and (B) at least one cetane improver.

2. A composition as claimed in claim 1 wherein the diesel detergent is an oil-soluble amide or imide of long chain hydrocarbyl substituted mono- and dicarboxylic acids or their anhydrides.

3. A composition as claimed in claim 1 wherein the diesel detergent is a long-chain hydrocarbyl monoamine or polyamine.

4. A composition as claimed in claim 3 wherein the diesel detergent is a long chain hydrocarbyl monoamine or polyamine of the formula

$$ABN(R^5N)_nR^4 \qquad IV$$

where A and B are independently hydrogen, a hydrocarbyl group of from 1 to about 10 carbon atom or a hydroxyhydrocarbyl group of from 1 to about 10 carbon atoms, and R^4 is an aliphatic hydrocarbon of from about 30 to 400 carbon atoms, R^5 is a divalent group and n is 0 or an integer from 1 to 7.

5. A composition as claimed in any one of claims 1 to 4 wherein the cetane improver is at least one of an alkyl nitrate, an ether nitrate, a dinitrate of a polyethylene glycol.

6. A composition as claimed in claim 5 wherein the cetane improver is at least one of isopropyl nitrate, isoamyl nitrate, isohexyl nitrate, cyclohexylnitrate or isooctyl nitrate.

7. A composition as claimed in claim 6 wherein the cetane improver is isooctyl nitrate.

8. A composition as claimed in any one of claims 1 to 7 wherein the composition further comprises a quaternary ammonium salt.

9. A diesel fuel composition comprising a major amount of a diesel fuel and a

minor amount of a fuel-soluble composition as claimed in any one of claims 1 to 8.

10. A composition as claimed in claim 9 wherein the diesel fuel is a middle distillate fuel boiling in the range 150 to 400°C, where at least 90% by volume of the fuel would be recovered on distillation at 350°C, at least 10% by volume would be recovered on distillation at 180°C, the aromatic content is less than 40% by volume and the cetane number is greater than 40.

11. A composition as claimed in either claim 9 or claim 10 wherein the sulphur content of the diesel fuel is less than 0.2%w/w.

12. The use of a composition as claimed in any one of claims 1 to 8 for reducing wear on cylinder liners, piston rings and rotary fuel injection pumps of diesel engines.

INTERNATIONAL SEARCH REPORT

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PCT/GB 96/00363

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C10L10/04 C10L1/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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P,X	DATABASE WPI Week 9527 Derwent Publications Ltd., London, GB; AN 95-204166 & JP,A,07 118 670 (COSMO) , 9 May 1995 see abstract ---	1,9,12
X	EP,A,0 476 196 (ETHYL) 25 March 1992 see the whole document ---	1,2,5,6, 8,9,11, 12
X	US,A,4 482 356 (HANLON) 13 November 1984 see the whole document ---	1,2,5-7, 9
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
29 March 1996	11 -04- 1996
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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